

The improved synthesis of carbonated soybean oil using supercritical carbon dioxide at a reduced reaction time†‡

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We have demonstrated an improved synthesis of a cyclic carbonate of soybean oil (CSO) utilizing supercritical carbon dioxide (CO₂) as the solvent. Because the mutual solubility of supercritical CO₂ and soybean oil is significantly higher than that of gaseous CO₂ and soybean oil, our method synthesizes the material in ~1/3 of the reaction time reported in the literature. We have also demonstrated a catalyst removal method for our system based on the simple Hofmann elimination reaction, reducing the need for organic solvent extraction. CSO is a potential petroleum replacement, and may be useful in the synthesis of polymers based on bio-resources.

Introduction

As petroleum prices surge to ~\$70/barrel,^{1,2} the use of bio-based alternatives continues to be necessary for both economic and environmental reasons. Energy absorbing materials from soybean oil are one area of high specific interest.^{3,4} Bio-based polyurethane foams have been developed with mechanical and thermoinsulating properties comparable to foams of petrochemical origin.^{5–8} These polymers are synthesized from soy based polyols and various di-isocyanates. One problem with these polymers is in making sure the di-isocyanate reacts completely as any unreacted isocyanate left in the polymer will react with ambient humidity and form voids in the material, reducing strength.⁸ The alternative synthesis using a carbonate pathway avoids this disadvantage.

There are several methods to prepare carbonates, with one of the most attractive being the catalyzed reaction between carbon dioxide (CO₂) and an epoxide. Using this reaction, polycarbonates have been formed from small epoxides such as propylene oxide^{9–11} and cyclohexene oxide.¹¹ Carbonates of oleochemical origin were patented as a plasticizing agent¹² and reported as a therapeutic agent¹³ more than 30 years ago. Older synthetic methods required environmentally unfriendly solvents and phosgene as a reactant. Recently, there has been renewed interest in a more environmentally friendly synthesis of carbonates^{14–16} brought on by a variety of new applications. Carbonates have physical and chemical properties which make them useful in the personal care, lubricant, fuel additive, and chemical feedstock industries.¹⁷ Shorter chain linear

carbonates are useful as emollients,¹⁴ where longer chain carbonates have been used as lubricants, plasticizers, and fuel additives.^{15,18} The cyclic carbonate, glycerol carbonate, has also found use as a highly polar solvent.^{14,18}

Conversion of various triglycerides and fatty acids to epoxides was reported by Swern ~60 years ago.^{19,20} Processes based on this reaction have been studied,^{21,22} improved^{23,24} and patented over the years,^{25–28} to the point where epoxidized soybean oil (ESO) is now available commercially. Other useful vegetable oil monomers have also been synthesized through an epoxide route.^{29–31} Following the epoxidation reaction, it is possible to form a cyclic carbonate with the addition of CO₂ and halide catalyst (Scheme 1).

The synthesis of carbonated soybean oil (CSO) has been reported by Tamami and co-workers, where they used CSO in the synthesis of polyurethanes.^{32,33} However, CSO could also be used as a synthetic building block for other products as well, including possible bio-based polyesters which may show better bio-degradation behavior than the polyurethane systems.³⁴ The longest step in Tamami's synthesis is the conversion of ESO to CSO with a reported conversion of 94% after 70 h. The reaction time in this step needs to be shortened for these materials to be commercially viable. Additionally, the catalyst is removed using an extraction method involving ethyl acetate. Herein we report that the synthesis of CSO can be accomplished in ~1/3 of the time reported in the literature by the use of supercritical CO₂. Further, we report two simple methods for catalyst removal which do not require organic solvent.

Results and discussion

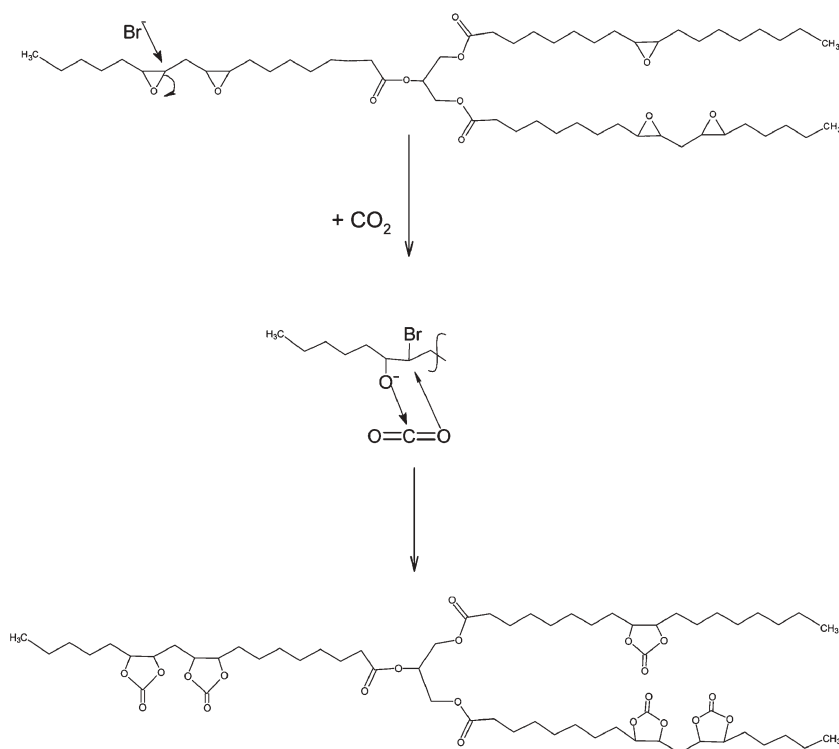
Carbonation of epoxidized soybean oil in supercritical CO₂

We synthesized CSO by reacting ESO with supercritical CO₂ at 100 °C with 5% (mol percent per oxirane moiety) catalyst. The reaction was run under 10.3 MPa of CO₂ for a variety of reaction times. The reaction was also attempted at 35 °C, however, no detectable reaction was observed at that temperature. The product from each of the successful reactions was studied by IR, ¹H NMR, and ¹³C NMR spectroscopy

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† Electronic supplementary information (ESI) available: Section S-1: The NMR data for carbonated soybean oil. Section S-2: A plot to obtain the apparent 1st order kinetic rate constant. See DOI: 10.1039/b511014a

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Scheme 1 The TBA^+Br^- catalyzed reaction on epoxidized soybean oil (ESO) to form carbonated soybean oil (CSO). There are an average of 4.2 oxirane moieties on each triglyceride.

(see ESI† Section S1), viscometry and thermogravimetric analysis (TGA).

Infrared spectra

The reaction products of the reaction at different reaction times were studied by IR spectroscopy. The IR spectra (Fig. 1) clearly show the conversion of ESO to CSO. The appearance of an additional band in the carbonyl region at 1793 cm^{-1} (C=O stretch) was the most apparent. It was larger than the carbonyl band associated with the triglyceride backbone as expected for the epoxy material with ~ 4.2 epoxides

per triglyceride. Also present is a new peak at 1047 cm^{-1} (C–O). The loss of epoxide bands at 823 cm^{-1} and 842 cm^{-1} indicates the consumption of the oxirane further confirming reaction. The inherent weakness of these epoxide bands does somewhat limit quantitation, so ^1H NMR and ^{13}C NMR spectroscopies were also used. Both the ^1H NMR and ^{13}C NMR spectra (see ESI† Section S1) show the conversion to the expected product in the 40 hour reaction time and about 82% conversion in the 10 h reaction sample.

Viscosity and gel permeation chromatography

The viscosity of the product was also studied. The materials synthesized ranged from a moderately viscous light brown oil to a darker brown very viscous and sticky material. This is consistent with the literature reports of this compound (Table 1).³³ However, to investigate the high viscosity, we ran solution gel permeation chromatography (GPC) of the product (Fig. 2). The resultant Mw (Table 1) was within error of the expected value of ~ 1123 Daltons. The highest concentration of any higher Mw material was only 2.5%.

Table 1 The measured extent of reaction, viscosity, and Mw of the carbonation reaction of ESO in supercritical CO_2 catalyzed by 5 mol% TBA^+Br^- catalyst at 100°C

Reaction time/h	% Reaction by ^1H NMR	Viscosity/Pa s–	Mw by GPC
0	0	0.396 ± 0.007	868
10	82	69.6 ± 6.9	1180
20	94	144.8 ± 6.8	1255
40	100	169.6 ± 12.0	1274

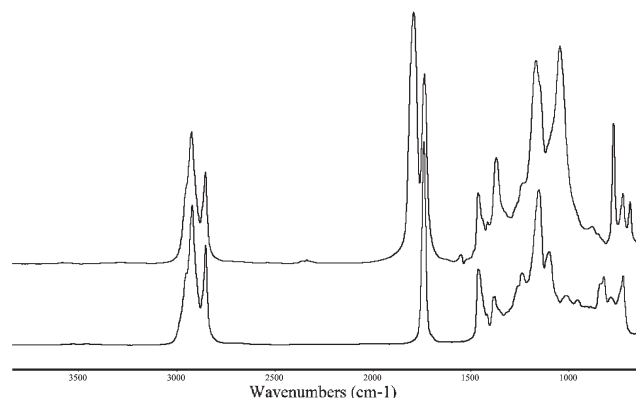


Fig. 1 The IR spectra of epoxidized soybean oil (ESO, lower spectrum) and carbonated soybean oil (CSO, upper spectrum). The disappearance of the spectroscopic peaks at $842\text{--}822\text{ cm}^{-1}$ shows the reaction progress. A new infrared spectroscopic peak at 1793 cm^{-1} shows the conversion to the carbonated product.

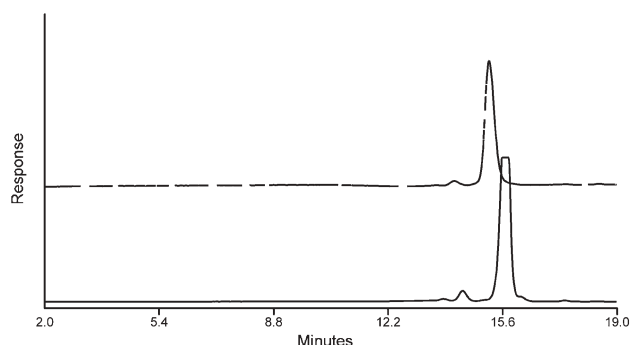


Fig. 2 The GPC analysis of CSO (top) and ESO (bottom). The GPC show that there is no significant polymerization formed during the carbonation reaction.

GPC of the starting material shows a similar amount (4.16%) of higher Mw material. There was clearly not sufficient polymerization to cause the noted viscosity increase. More likely, the viscosity increase is caused by the polar interaction of the carbonate moiety. This phenomenon has been recently observed and modeled for acrylated triglycerides, including soybean oil,³⁵ where Arrhenius viscosity behavior is observed.

Discussion of the reaction rate enhancement in supercritical carbon dioxide

There are two explanations for the observed rate enhancement in supercritical CO₂. The first hypothesis for the rate enhancement is the formation of a CO₂ expanded liquid,³⁶ which would reduce the viscosity of the oil increasing the diffusion of the reactant CO₂.³⁷ Although this would easily explain the rate enhancement shown in this work, there were no observations consistent with the expanded liquid formation. The second simpler hypothesis is a solubility effect. The mutual solubilities of CO₂ and the oil have been studied in the literature^{38–40} and shown to vary significantly with both pressure and temperature. Solubility parameters for CO₂ with a variety of oils and other liquids have been estimated.⁴¹ Non-polar liquids, such as soy oil, jojoba oil, and castor oil, have mutual solubilities which increase with increasing pressure. Soybean oil and supercritical CO₂ are considered completely miscible at 80 °C and at 95.0 MPa.⁴² The solubilities of fatty materials at the pressures used in our system have also been studied in the literature. For example, the solubility of a fish oil ethyl ester in supercritical CO₂ at 5.13 MPa and 70 °C is 0.064 Nm³ kg^{−1}. When the pressure is increased to 10.04 MPa maintaining constant temperature, the solubility increases almost three fold to 0.170 Nm³ kg^{−1}.⁴⁰

Table 2 The catalysts studied for the carbonation of ESO in supercritical CO₂ at 100 °C with a 40 h reaction time. Only the TBA⁺Br[−] system showed significant reactivity

Reaction catalyst (0.5 mol%)	% Reaction by ¹ H NMR
None	0
TBA ⁺ Br [−]	100
K ⁺ Br [−]	6
Li ⁺ Br [−]	0
TBA ⁺ OH [−]	0

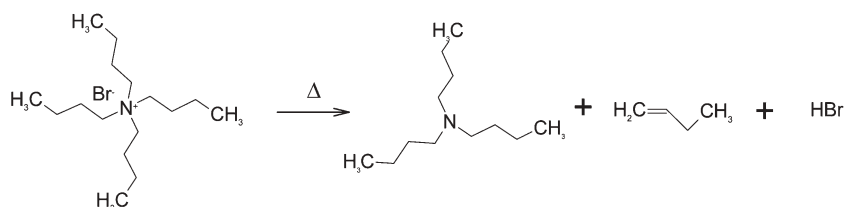
Because we ran the system at constant CO₂ concentration, an apparent 1st order kinetic rate constant can be calculated from a plot kinetic plot of ln [ESO]_{initial}/[ESO]. A value of 0.1118 h^{−1} was calculated, giving a *t*_{1/2} of 6.2 h (see ESI† Section S-2). From literature synthesis, a rate of ~0.0402 h^{−1} and *t*_{1/2} of 17.2 h can be calculated in a similar manner. In other words, we have increased the observed reaction rate by a factor of three. This closely matches the expected difference in the mutual solubility of the reactants and can explain the enhanced rate.

Other catalysts

We ran similar experiments with a variety of other catalysts in order to determine if the TBA⁺Br[−] salt was necessary for the reaction (Table 2). We used TBA⁺OH[−] solution, Li⁺Br[−], and K⁺Br[−] all at 5 mol% as well as a catalyst free system. Both ¹H NMR and IR of the resultant products were taken, and all of these systems showed little or no reactivity. This is especially interesting in the Li⁺Br[−] case where reactivity has been shown in other carbonate systems.^{43,44} The lack of activity is probably due to poor solubility of these catalysts in both the epoxidized soybean oil and in supercritical CO₂. Further catalyst studies for CO₂ soluble systems of higher reactivity may be of interest, as was found in polymerization^{45,46} and hydrogenation reactions.⁴⁷ However, the TBA⁺Br[−] system has an advantage in that it can be removed by thermal breakdown into volatile products by the Hofmann elimination reaction (Scheme 2).

Catalyst removal and TGA analysis

In order to take advantage of the catalyst breakdown reaction, we heated the material with catalyst still present (Fig. 3), and noticed a temperature where the catalyst breakdown occurs but the carbonated oil product is still stable: 190 °C. We treated material at this temperature under a nitrogen atmosphere for 2 hours. The material lost the expected 8.6% mass within error of the 7.5% observed in the TGA experiment. The volatile mass lost from the sample was trapped and determined



Scheme 2 The well studied Hofmann elimination of TBA⁺Br[−] under heating. TGA analysis of pure material shows complete catalyst removal by this decomposition to volatile products which occurs from 150–190 °C.

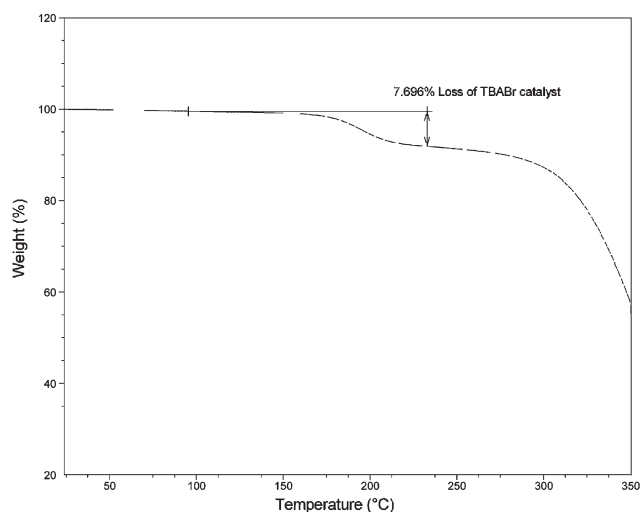


Fig. 3 The TGA trace of CSO with catalyst still present. The initial loss of material, ~8%, is evidence of the decomposition of the catalyst (TBA^+Br^-) to volatile material.

to be the expected tributylamine by GC analysis and comparison to a standard solution. The resultant CSO was compared and found to be identical to CSO which had catalyst removed by a washing and sonication method. TGA analyses of both samples (Fig. 4) show identical behavior, and ^1H NMR analysis confirmed complete removal of the catalyst. It is of note that the oil stability is not a complicating issue as the temperature employed here is significantly below the 288–306 °C temperature where thermal decomposition⁴⁸ of vegetable oil occurs and well below the 325–335 °C preferred for thermal viscosity modification of soybean oil.^{49,50}

Overall, our synthesis is a step in making a potentially useful chemical material available for use. The potential to use the Hofmann reaction allows for an easy catalyst removal mechanism, or the material can be washed and the catalyst

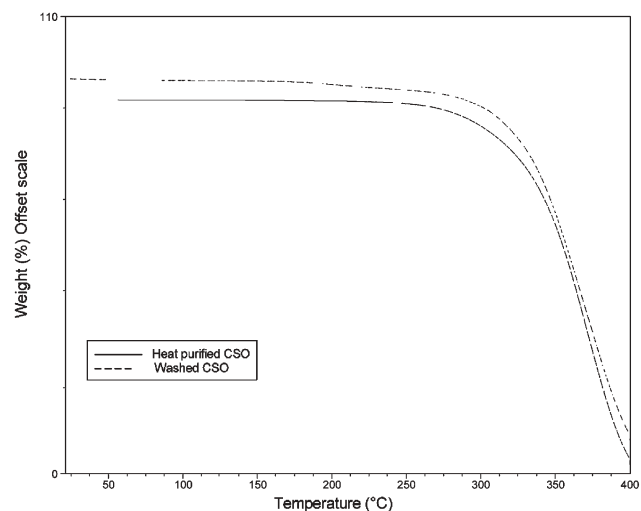


Fig. 4 The TGA traces for samples of CSO which have had catalyst removed by washing and sonication (top) and by heat purification (bottom). The material shows no change with respect to the different purification methods.

reused. The potential of using supercritical CO_2 in a continuous flow system for carbonation of propylene oxide has been demonstrated.⁴³ Extension of this type of reaction to oleochemical epoxides may allow the synthesis of a variety of useful materials. Further work may include trying this reaction at even higher pressure to further reduce the reaction time.

Experimental

Materials

Epoxidized soybean oil (Atofina, VIKOFLEX 7170, 4.2 oxirane moieties per triglyceride); tetrabutylammonium bromide (Sigma, 99%); tetrabutylammonium hydroxide (Sigma, ACS reagent); potassium hydroxide (Barns, Analytical); lithium hydroxide (Sigma-Aldrich, 99%); carbon dioxide (AirGas 50 lb syphon type high pressure cylinder, UN1013); tetrahydrofuran (Sigma-Aldrich, 99 + % ACS reagent); and tributylamine (Fluka, >99.0%) were used as received.

Instrumentation and equipment

The reactor employed was a Parr 4560 mini benchtop controlled by a thermocouple equipped Parr 4843 controller. A 300 mL reactor body equipped with quartz viewing windows was used.

FTIR spectra were recorded on a Thermo Nicolet Nexus 470 FTIR with a Smart ARK accessory containing a 45° ZeSe trough. Data were collected and processed on a Windows 2000 equipped Dell Optiplex GX260 Pentium 4, 2.46 GHz computer running Omnic 6.2 software.

Gel permeation chromatography was performed on a Polymer Labs PL-GPC 120 high temperature chromatograph through a Polymer Labs PLgel 5 μm guard (50 \times 7.5 mm) and 2 Polymer Labs PLgel 3 μm MIXED-E (300 \times 7.5 mm) columns using a Refractive Index detector. A Holland spark Midas autosampler was employed. Data were collected and processed on a Windows 98 Micron Pentium 2 computer running Cirrus GPC online GPC/SEC software version 1.11. Chromatographic runs were made using an isocratic flow rate (1 mL min^{-1}) of tetrahydrofuran at 40 °C. The Mw were calculated by the Cirrus software using a third order polynomial derived from a standard curve. The standard curve was generated from a series of polystyrene Mw standards (Polymerlabs easycal A) and a series of mono, di, and tri oleins and palmitates (Nu-Chek Prep, Inc.)

NMR spectroscopy (See ESI† Section S-1) was performed on a Bruker Avance 500 NMR. It was operating at 500 MHz for ^1H and 125 MHz for ^{13}C . Viscosity measurements were performed on a TA Instruments ARES controlled strain rheometer with 1 K FRTN1 transducer using TA Orchestrator software package 7.0.

Viscosity was measured at 25 °C using a rate sweep method where the shear rate was increased until a constant viscosity was measured. The shear rate had to be varied from 0.1 s^{-1} to 500 s^{-1} depending on the sample studied.

Freeze drying was performed with a Labconco Freezone 1. Samples were pre-frozen in a dry ice/ethanol bath using standard laboratory procedures.

Thermogravimetric analysis (TGA) was performed on a TA TGA Q500. Data were collected and processed on a Windows 2000 × 86 Family6 Model 8 IBM computer with Advantage for Q series version 1.5.0.208 Thermal Advantage release 3.2.0 software. Samples were heated under nitrogen using a heating ramp of 2.0 °C min⁻¹ from 25 °C to 350 °C.

Gas chromatography was performed on a Hewlett Packard 6890 GC system equipped with a 6890 series injector and a 5973 mass detector. Samples were collected using a solid phase micro-extraction PDMS fiber over the headspace of the trapped sample for 1 h.

Synthesis of carbonated soybean oil

Epoxidized soybean oil (ESO) was heated in a warm water bath until fluid and ~30 g (0.0311 mol triglyceride, 0.131 mol of oxirane functionality) poured into a 300 mL high pressure reactor vessel. Next, ~2.11 g (0.0065 mol, 5.0 molar percent, 6.6 weight percent) tetrabutylammonium bromide (TBA⁺Br⁻) was dissolved into the oil with stirring. The reactor was closed and pressurized with CO₂ to ~3.4 MPa. The reactor was then heated to 100 °C causing the pressure to rise. Once the reaction temperature was reached, the CO₂ pressure was further increased to 10.3 MPa and maintained there throughout the reaction with the necessary addition of CO₂ by the pressure controlling pump. After the reaction time was complete, the reactor was de-pressurized slowly to allow dissolved CO₂ to leave the carbonated product. Typical isolated yield was ~29 g, ~81% based on a product of Mw 1150 g mol⁻¹, with the loss caused by difficulty in recovering the viscous light brown liquid from the reactor.

Removal of tetrabutylammonium bromide from the product

Catalyst removal could be accomplished by either of the following two methods. The first allows the recovery, characterization, and possible reuse of the catalyst, the second method takes advantage of the Hofmann elimination reaction possible for TBA⁺Br⁻. In the first method, 5 g of carbonated soybean oil was suspended in ~50 mL of warm (50 °C) water. The mixture was sonicated for two hours in order to obtain a dispersion. After sonication, the mixture was separated using a separatory funnel, and the process repeated two more times. All of the water washings were saved and freeze dried yielding 0.308 g (96% recovery) of white powder. This white powder was verified to be TBA⁺Br⁻ by NMR and TGA analysis. The carbonated soybean oil solution was dried in a Kugel-Rohr[®] and characterized by IR (Fig. 1) and TGA (Fig. 3) as well as by ¹H NMR, ¹³C NMR (see ESI† Section S-1). The second method of catalyst removal involved heating of the carbonated soybean oil to 190 °C for ~2½ hours. TGA analysis shows that the carbonated soybean oil is stable at this temperature, however the catalyst decomposes into volatile Hofmann elimination products which are removed in the nitrogen stream. The volatile products were trapped in a dry ice/ethanol trap and verified to be the expected tributylamine by GC analysis. The final product was comparable to the washed product by TGA, IR, and ¹H NMR spectroscopy.

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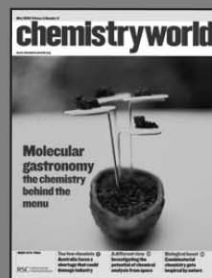
References

- 1 P. Van Arnum, *Chem. Mark. Rep.*, 2004, **266**, 1.
- 2 P. Viswanathan, *Chem. Mark. Rep.*, 2005, **267**, 1.
- 3 Z. S. Liu and S. Z. Erhan, The United States-Japan Cooperative Program in Natural Resources Food and Agricultural Panel, Tsukuba, Ibaraki, Japan, 2003, p. 394.
- 4 S. N. Khot, J. J. Lascala, E. Can, S. S. Morye, G. I. Williams, G. R. Palmese, S. H. Kusefoglu and R. P. Wool, *J. Appl. Polym. Sci.*, 2001, **82**, 703.
- 5 A. Guo, I. Javni and Z. Petrovic, *J. Appl. Polym. Sci.*, 2000, **77**, 467.
- 6 I. Javni, Z. S. Petrovic, A. Guo and R. Fuller, *J. Appl. Polym. Sci.*, 2000, **77**, 1723.
- 7 I. Javni, W. Zhang and Z. S. Petrovic, *J. Appl. Polym. Sci.*, 2003, **88**, 2912.
- 8 S. Husic, I. Javni and Z. S. Petrovic, *Compos. Sci. Technol.*, 2005, **65**, 19.
- 9 K. Yamaguchi, K. Ebitani, K. Kaneda, T. Yoshida and H. Yoshida, *J. Am. Chem. Soc.*, 1999, **121**, 4526.
- 10 M. H. Chisholm and Z. Zhou, *J. Am. Chem. Soc.*, 2004, **126**, 11030.
- 11 S. D. Thorat, P. J. Phillips, V. Semenov and A. Gakh, *J. Appl. Polym. Sci.*, 2003, **89**, 1163.
- 12 W. I. Riedeman, Carbanato Esters of Fatty Acids, *US Pat.*, 2826591, Mar. 11, 1958.
- 13 A. D. Bender, C. E. Berkoff, W. G. Groves, L. M. Sofranko, G. R. Wellman, J.-H. Liu, P. P. Begosh and J. W. Norodniak, *J. Med. Chem.*, 1975, **18**, 1094.
- 14 M. Dierker, *Lipid Technol.*, 2004, **16**, 130.
- 15 J. A. Kenar, *INFORM*, 2004, **15**, 580.
- 16 J. A. Kenar and I. D. Tevis, *Eur. J. Lipid Sci. Technol.*, 2005, **107**, 135.
- 17 J. A. Kenar, G. Knothe, R. O. Dunn, T. W. I. Ryan and A. Matheaus, *J. Am. Oil Chem. Soc.*, 2005, **82**, 201.
- 18 J. A. Kenar, G. Knothe, A. L. Copes and J. A. Kenar, *J. Am. Oil Chem. Soc.*, 2004, **81**, 285.
- 19 D. Swern, G. N. Billen, T. W. Findley and J. T. Scanlan, *J. Am. Chem. Soc.*, 1945, **67**, 1786.
- 20 T. W. Findley, D. Swern and J. T. Scanlan, *J. Am. Chem. Soc.*, 1945, **67**, 412.
- 21 A. Campanella, M. A. Baltanás, M. C. Capel-Sánchez, J. M. Campos-Martín and J. L. G. Fierro, *Green Chem.*, 2004, **6**, 330.
- 22 A. Campanella and M. A. Baltanás, *Eur. J. Lipid Sci. Technol.*, 2004, **106**, 524.
- 23 R. E. Harry-O'Kuru, R. A. Holser, T. P. Abbott and D. Weisleder, *Ind. Crops Prod.*, 2002, 51.
- 24 K. D. Carlson, R. Kleiman and M. O. Bagby, *J. Am. Oil Chem. Soc.*, 1994, **71**, 175.
- 25 G. L. Crocco, W. F. Shum, J. G. Zajacek and H. S. J. Kesling, Epoxidation Process, *US Pat.*, 5166372, 1992.
- 26 W. F. Shum and H. S. J. Kesling, Olefin Epoxidation using a Perphenate Catalyst and an Organic Hydrogenperoxide, *US Pat.*, 5118822, Jun. 2, 1992.
- 27 J. A. Nowak, T. A. Zillner, I. Mullin and L. Patrick, Thin-film Epoxidation of an Unsaturated Oil or Alkyl Fatty Acid Ester, *US Pat.* 6734315, May 11, 2004.
- 28 J. A. Nowak, T. A. Zillner, I. Mullin and L. Patrick, Thin-film Epoxidation of an Unsaturated Oil or Alkyl Fatty Acid Ester, *US Pat.* 6740763, May 25, 2004.
- 29 S. P. Bunker and R. P. Wool, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, 451.
- 30 J. La Scala and R. P. Wool, *J. Am. Oil Chem. Soc.*, 2002, 373.
- 31 J. Lu, S. Khot and R. P. Wool, *Polymer*, 2005, **46**, 71.

- 32 G. L. Wilkes, S. Sohn and B. Tamami, Preparations of nonisocyanate polyurethane materials from epoxidized soybean oils and related epoxidized vegetable oils, *US Pat.*, 2004074352, Feb. 19, 2004.
- 33 B. Tamami, S. Sohn, G. L. Wilkes and B. Tamami, *J. Appl. Polym. Sci.*, 2004, **92**, 883.
- 34 R. L. Shogren, Z. Petrovic, Z. Liu and S. Z. Erhan, *J. Polym. Environ.*, 2004, **12**, 173.
- 35 J. La Scala and R. P. Wool, *J. Appl. Polym. Sci.*, 2005, **95**, 774.
- 36 Z. Liu, D. Li, G. Yang and B. Han, *J. Supercrit. Fluids*, 2000, **18**, 111.
- 37 B. Kerler, B. Subramaniam, R. E. Robinson and A. S. Borovik, *Appl. Catal., B*, 2004, **49**, 91.
- 38 K. D. Bartle, A. A. Clifford and S. A. Jafar, *J. Chem. Eng. Data*, 1990, **35**, 355.
- 39 D. J. Miller, S. B. Hawthorne, A. A. Clifford and S. Zhu, *J. Chem. Eng. Data*, 1996, **41**, 779.
- 40 A. Staby and J. Mollerup, *J. Am. Oil Chem. Soc.*, 1993, **70**, 583.
- 41 R. L. Eissler and J. P. Friedrich, *J. Am. Oil Chem. Soc.*, 1988, **65**, 764.
- 42 F. Temelli, J. W. King and G. R. List, *J. Am. Oil Chem. Soc.*, 1996, **73**, 699.
- 43 T. Sako, T. Fukai, R. Sahashi, M. Sone and M. Matsuno, *Ind. Eng. Chem.*, 2002, **41**, 5353.
- 44 T. Sako, T. Sugeta, N. Nakazawa, K. Otake, M. Sato, K. Ishihara and M. Kato, *Fluid Phase Equilib.*, 1995, **108**, 293.
- 45 G. W. Coates and D. R. Moore, *Angew. Chem., Int. Ed.*, 2004, **43**, 6618.
- 46 C. M. Byrne, S. D. Allen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2004, **126**, 11404.
- 47 P. G. Jessop, Y. Hsiao, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.*, 1996, **118**, 344.
- 48 J. Dweck and C. M. S. Sampaio, *J. Therm. Anal.*, 2004, **75**, 385.
- 49 S. Z. Erhan and M. O. Bagby, Vegetable Oil-based Offset Printing Inks, *US Pat.*, 5713990, Feb. 3, 1998.
- 50 S. Z. Erhan, Q. Sheng and H.-S. Hwang, *J. Am. Oil Chem. Soc.*, 2003, **80**, 177.

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